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SS-SPECTROMETRIC OBSERVATIONS ON  
(ETHYLMERCURI)-p-TOLUENESULFANILIDE,  
ESAN-M

Leonard I. Katzin and Martin H. Studier



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MASS-SPECTROMETRIC OBSERVATIONS ON  
N-(ETHYLMERCURI)-p-TOLUENESULFANILIDE,  
CERESAN-M

by

Leonard I. Katzin and Martin H. Studier

Chemistry Division

May 1971



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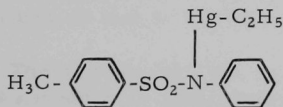
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ABSTRACT

In the mass spectrometer, N-(ethylmercuri)-p-toluenesulfanilide shows the parent ion as the only mercury-bearing entity (mass 477 for  $^{202}\text{Hg}$ ). The main fragment is mass 246, formed by the loss of neutral  $\text{C}_2\text{H}_5\text{Hg}$ . Ceresan-M, heated to fusion in a closed system and cooled, now shows largely the mass spectrum due to  $\text{Hg}(\text{C}_2\text{H}_5)_2$ . The commercial product for seed treatment, 7% Ceresan-M in starch, gives the same results. It seems probable that in human poisoning cases involving grain treated with Ceresan-M,  $\text{Hg}(\text{C}_2\text{H}_5)_2$  and related compounds formed by reaction of  $\text{Hg}(\text{C}_2\text{H}_5)$  radical with the mix must be considered as important toxic agents.

INTRODUCTION

N-(ethylmercuri)-p-toluenesulfanilide, the mercurial



known commercially as Ceresan-M, is used to control smuts and fungi of seed grain, particularly wheat. In this use, it is supplied as a 7% mixture with starch.

As with other mercurials, Ceresan-M has been the agent of accidental human poisonings.<sup>1</sup> Of particular interest for this report is a series of fatal poisonings of Iraqi farmers and their family members.<sup>2</sup> In these cases, wheat preserved with Ceresan-M, meant for seed use only, was mixed with untreated grain and baked into bread. The detailed pathology of these victims presented features not entirely compatible with expectation from the nominal toxic agent<sup>2</sup> and prompted further investigation. More information on the chemistry of Ceresan-M was deemed essential. Since the compound has an odor ascribed to it, a presumption of some volatility was reasonable, so we considered it appropriate to invoke the aid of the



## PROCEDURES

Samples of the technically pure Ceresan-M, and of the commercial product consisting of a 7% mixture with starch, were kindly supplied to us by Dr. James C. Daniels, M.D.

The instrument used was the Bendix time-of-flight mass spectrometer, modified so that oscilloscopic monitoring, photography of the oscilloscopic trace, and paper-strip-chart recording of the spectra could be used as desired.<sup>3</sup> Both external glass sample tubes, connected to the ion source of the instrument through a metal tube and needle valve, and internal filament sources, were used as appropriate.

## RESULTS

A cold sample of the Ceresan-M placed on a filament in the mass spectrograph showed essentially instrumental background. When the filament is warmed, a characteristic pattern developed. Only one significant component of this pattern showed the presence of mercury as an ingredient atom, and that is the parent peak, mass 477 for  $^{202}\text{Hg}$ . The most abundant fragment was about mass 246, corresponding to the elimination of  $\text{C}_2\text{H}_5\text{Hg}$  from the parent. There was also a lesser peak at mass 275, corresponding to elimination of the mercury atom alone.

Further fragmentation derivatives of the mass 246 ion are seen: masses 181 and 182 (elimination of  $\text{SO}_2$  and  $\text{HSO}_2$ ); mass 167 (loss of  $\text{C}_6\text{H}_5$ ); mass 154 (loss of either  $\text{CH}_3\text{C}_6\text{H}_4$  or  $\text{NC}_6\text{H}_5$  of same mass number); masses 91-92 (toluene pattern); and masses 64-66. Lighter masses and minor components were not investigated. Some of the ions indicated may have gained or lost a hydrogen mass.

The pattern for  $\text{C}_2\text{H}_5\text{Hg}$  expected to accompany the mass 246 fragment is not visible. This suggests that the  $\text{C}_2\text{H}_5\text{Hg}$  separates off as an uncharged entity on decomposition of the parent Ceresan-M. Further relevant evidence is discussed below.

If the Ceresan-M is placed in a sample tube connected to the spectrometer source through a brass valve and connections, and the tube is warmed gently, an increase is seen in the mercury intensity above background, and in the  $\text{C}_2\text{H}_5$  pattern. Heavy ions are not seen. This would be consistent with decomposition of the Ceresan-M on the metal and passage of  $\text{C}_2\text{H}_5\text{Hg}$  into the ionization chamber, where it is decomposed to  $\text{Hg}^+$  and  $\text{C}_2\text{H}_5^+$  or  $\text{C}_2\text{H}_4^+$ .

Heating the material in the external tube to fusion brings on reaction, with evolution of more volatile material from a less volatile matrix.





After the tube is cooled, the spectrum is now dominated by  $\text{Hg}(\text{C}_2\text{H}_5)_2^+$  and  $\text{Hg}(\text{C}_2\text{H}_5)^+$  (probably mixed with  $\text{Hg}(\text{C}_2\text{H}_4)^+$ ), in what would seem to be the pattern typical for diethyl mercury. The cold external sample tube contains droplets of liquid, which could be diethyl mercury. Formation of this substance can be considered confirmation for the presence of  $\text{HgC}_2\text{H}_5$  in the primary decomposition of the Ceresan-M.

The commercial seed fumigant, about 7% Ceresan-M in starch, gives the same behavior in the external tube as does the undiluted mercurial.

It seems reasonable to conclude that in the poisoning cases reported in consequence of consumption of bread made from wheat treated with Ceresan-M, one probable mercurial agent, among others possible, is diethyl mercury. This would explain similarity in symptoms and pathology to those in the Japanese fish poisoning cases ("Minamata disease").<sup>4,5</sup> There might be some residual parent Ceresan-M, and possibly some more complex derivative from the  $\text{C}_2\text{H}_5\text{Hg}$  radical, to complicate the details of the pathology.

#### ACKNOWLEDGMENT

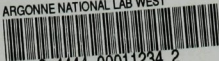
We are deeply indebted to Dr. Daniels for calling this problem to our attention, and for supplying us with the samples of Ceresan-M.

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